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Removal of Heavy Metals and Dyes from Wastewater and Industrial Effluents: A Review on Capacities and Efficiencies of Nanomaterials.

John Godwin[1] and Omale O. Innocent[2]

[1]Department of Chemistry, Kogi State College of Education (Technical) Kabba, Kogi State, Nigeria
[2]Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi State, Kogi State College of Education Study Centre, Ankpa, Nigeria.

Abstract

Heavy metal and dyes are among the major pollutants of the environment and the need to constantly monitor the water body is of paramount importance. In recent times, the uses of nanomaterials have attracted the attention of Researchers globally. In this review, the use of nanomaterials as adsorbent was examined with respect to their removal of heavy metals and dyes from wastewater and industrial effluents. The adsorptive performance of these nano-sized materials in terms of capacities and efficiencies, and factors that determine adsorption such as pH, contact time and adsorbent dosage in various studies were reviewed. The models which explain the interaction between the adsorbent and adsorbate (Adsorption isotherms) and the rate of adsorption (Adsorption Kinetics) were also examined. It was found that, on the average, nanomaterials were found to be over 80% efficient as adsorbent of heavy metals and dyes.

Key words: Adsorbent, Dye, Heavy metals, Industrial Effluent, Nanomaterials, Wastewater.

1.0 Introduction

Over the years, the environment has suffered a great deal of increased contaminants which ranges from deposition of pollutants like heavy metals and dyes directly or indirectly into water bodies from chemical industries. The increase in human activities such as indiscriminate sewage disposal and discharge of domestic and industrial waste into rivers and streams are a major contributing factors to the wide spread of these pollutants into the environment in Nigeria and other parts of the world

Industries that utilize dyes and discharge them as pollutants include textile, paper, paint, leather etc. The rise in the concentration of heavy metals in water bodies is of immediate concern to environmental scientists due the toxic nature of some of these metals. These indiscriminate waste disposal practices have lead to the accumulation of heavy metals in aquatic animals which indirectly affect man as he feeds directly on these animals.

Report showed that disposal of sewage in the range of about 2900MLD from cities and towns is the greatest source of pollution of water bodies in some parts of the world such as India, and an estimated 70% of water pollution in the Maharashtra is as a result of domestic sewage disposal [1]. The present annual world production of lead (Pb) is about 5.4 million tons and continues to increase and such chemical industries continue to pose a great risk to the life of workers as well as the surrounding environment [2]. Contaminant such as methyl violet could hinder the growth of bacteria and processes such as photosynthesis of aquatic plants. Dyes such as methyl blue may be harmful by injection, inhalation and contact with skin. It has been estimated that the total consumption of dyes in textile industries worldwide is greater than 10,000 tons per year and about 10-15% of these dyes are released as effluents into the environment during dyeing processes which eventually contaminate their destination. These dyes invariably remain in industrial waste as pollutants [3].

Various acute and chronic diseases have emerged as a result of direct or indirect intake of infected or contaminated food by man beyond the safe limit. Therefore, it is very important for environmental analysts to continue monitoring of the environment to save human and plants from the destructive effects of these pollutants. In view of this, the preparation, manipulation and application of nanomaterials have been extensively studied and used in recent times to remove pollutants from water and industrial wastes. Nanotechnology has been utilized to design and prepare materials to provide an economical, convenient and eco-friendly means of water remediation.

2.0 Nanomaterials (NMs)

Nanotechnology is the synthesis and manipulation of organic and inorganic materials for use in a particular application through certain chemical or physical processes to synthesize materials having nanosized dimension in the range of 1 - 100 nm with the specific properties [4]. Nanomaterials with distinct characteristics can be synthesized from bulk materials by bringing various substances with designed properties together. Recent studies in nanoscale science and engineering suggest that most of the current problems involving environmental issues such as water quality could be resolved or greatly reduced by NMs [5]. The technology is now used widely in industries that utilize dyes, pharmaceutical industries, medical science, electronics, robotics, tissue engineering, water treatment etc. Nanoparticles, nanomembrane and nanopowder are used currently for detection and removal of chemical and biological substances, metals (eg Cadmium, Copper, Lead, Mercury, Nickel, Zinc), nutrients (Phosphate, Ammonia and Nitrate), Cyanides, Organics, Algae (e.g., Cyanobacterial toxins, Viruses), Bacteria, Parasites and Antibiotics etc. [6].

There are basically four classes of nanoscale materials that are been utilized as functional materials for water purification; metal containing NMs e.g., nanogold, nanosilver, metal oxides (e.g., NiO, TiO, ZnO, Fe_2O_3 etc), Carbonaceous NMs containing mainly carbon inform of nanotubes (cylindrical), fullerenes (spherical and ellipsoidal), Dedrimers are nanosized polymers build from branched units which are mostly used as catalyst and, Composite nanoparticles are combined with other nanoparticles. Nanoparticles such as nanosized clays are added to enhance mechanical, thermal, barrier and flame retardant properties [4].

2.1 Superparamagnetism of Nanomaterials

NMs have numerous distinct properties most especially magnetization behaviour which is different from the bulk material. In case of magnetic properties of nanoparticles, the change which occurs in nanoscale is superparamagnetism. This phenomenon occurs in ferro- and ferrimagnetics, after decresasing their particles sizes to nanoscale (10 – 100nm) [7]. Current studies have diverted attention to the use of nanosized magnetic materials which have attracted growing interest as a result of their increased surface area and superparamagnetism [9]. Decrease in size of magnetic materials (multi-domain materials) leading to the formation of single-domain particles also results to the phenomenon of superparamagnetism [8].

2.2 Stabilization of Nanomaterials

NMs can be stabilized when undergoing synthesis to checkmate oxidation and agglomeration which are largely due to high surface area and chemical reactivity. Under ambient condition, rapid oxidation of NMs surface take place, leading to occurence of thin oxide layer that dramatically changes the properties of NMs. To preserve their magnetic properties and shield nanoparticles from oxidation and agglomeration, encapsulation of the NMs have been successfully designed and employed using silicon, precious metals, metal oxide, carbon, organic polymers, surfactants etc. [8].

2.3 Regeneration of Nanomaterials

Regeneration is the recovery of NMs after use. It has been studied extensively in various works and adsorption mechanism has been found to have direct impact on feasibility of regeneration of magnetic nanoparticles. Also, chemical adsorption can decrease regeneration but can be overcome by surface modification or coating to prevent magnetic core from redox reaction and chemical adsorption [9].

2.4 Characterization of Nanomaterials

The properties of NMs such as physicochemical properties are very important for their behavior, bio-distribution, safety, and efficacy if they must perform to espection [10]. In other-words, characterization of NMS is important in order to evaluate the functional aspects of the synthesized particles. Characterization is performed using a variety of analytical techniques, including X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), UV-vis spectroscopy [10]. Properties of NMs are largely determined by their surface area, particles size, morphology, structure, surface functional groups, surface reaction, and volume and pore size etc.

3.0 Heavy Metals as Pollutants and Sources

Heavy Metals are group elements which have atomic mass between 63.50 and 200.60 and a specific gravity greater than 5.00 (Dimple, 2014). They includes Nickel (Ni), Chromium (Cr), Copper (Cu), Cadmium (Cd), Cobalt (Co), Zinc (Zn), Lead (Pb), Arsenic (As), Silver (Ag) etc. They pose a great health threat to human life and plant growth when in a high concentrations in the environment especially the water body. Those found in industrial effluents includes Ni, Cr, Pb, Ar and Cd [12]. Since most of the industrial wastewater is discharged directly into the rivers without treatment, heavy metals are major pollutants in marine, ground, industrial and even treated water. Post sources of these heavy metal pollutants are industrial wastewater from metal processing tanneries, pharmaceuticals, pesticides, dyes, organic chemicals, rubber, plastic, lumber wood products and mining etc.

These heavy metals are transported by runoff water and contaminated water sources downstream from industrial waste [11].

3.1 Adsorption of Heavy Metals by Nanomaterials

Adsorption has been applied in different works for the removal of heavy metals (table 1.0). Among numerous methods such as redox reaction, photocatalysis, Complexation, ion exchange, solvent extraction, membrane operation, coagulation, chemical precipitation and electro-deposition, Adsorption method is considered as a user-friendly, very effective and separation method for the removal of heavy metals from wastewater with the advantages of specific affinity, easy accessibility, low cost and simple design [13]. Many oxides and carbon-based NMs where reported in literature as adsorbent for the removal of heavy metals such as Ni^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Sr^{2+}, Zn^{2+} and U^{6+} from industrial wastewater and polluted aquatic sources [14]. Hexavalent chromium have been removed from aqueous solution using magnetic nanoparticles coated with alumina and modified by Cetyl Trimethyl Ammonium

Bromide and the modified nanoparticle was demonstrated to be 95% efficient [15]. In a different analysis on Copper (II) removal by Pectin-Iron oxide magnetic nanocomposite, pectin-coated magnetic composite was shown to be effective in removal of copper [16]. In the study of adsorption of Pb(II) on Iron oxide nanoparticles immobilized Phanerochaete Chrysponium, the adsorption-desorption studies showed that the prepared adsorbent kept its adsorption ef

Table 1.0: Nanaomaterials and their adsorption capacities at different conditions for various metal ions adsorption

S/N	Nanaomaterial	Analyte	pH	Temperature (^0C)	Adsorption time	Adsorption (%)	Adsorption capacity (mg/g)	Reference
1	Alumina/Iron Oxide nano-composite	Cd2+	6	55	300 min	X	625	[27]
2	ZnO-PLLA nanofibre composite	Cr(VI)	3.5	X	1300 min	60	X	[38]
3	Alumuna	Zn(II)	7	45	4.5 hrs	35.5	473.83	[35]
4	Magnetic Iron oxide nano-particles stabilized with oils	Cu2+, Ni2+, Cr2+	2.5	30	6 hrs	90	x	[39]
5	Nanoscale zerovalent Iron Supported on mesoporous silica	Cr(VI)	3	X	12 hrs	100	x	[41]
6	Novel zerovalent Iron na-noparticles	Cu2+	6	X	60 min	86.3	x	[33]
7	Magnetic nanoparticles	As(III)	7	22.5	3 min	82	23.8	[5]
8	CuO nanoparticle	Cr(VI)	6.5	27	X	60	19.61	[40]
9	Nanosized magnetite mod-ified with SDS	Cr(VI)	4	30	60 min	99.7	x	[45]
10	Ferrite nanoparticles	C2+, Cd2+, Pb2+	6	X	1 min	X	136	[34]
11	Pectin-Iron oxide magnetic composite	Cu2+	5	25	x	X	48.89	[16]
12	Maghetite nanoparticles	Zn2+,	2.5	X	20 min	96	15	[32]

		Cu2+, Cd2+						
13	$NiFe_2O_4$ nanoparticles	Pb2+	9	29	2 hrs	99	168	[20]
14	Iron oxide immobilized phanerochaete-chryscoporium	Pb2+	5	35	60 min	90	176.33	[18]
15	Fe3O4 magnetic polymer microspere functionalized with amino group	Cr(VI)	2	25	120 min	X	253	[44]

X = undocumented

ficiencies constant over 5 cycles at about 90% [18]. In a further study, removal efficiency on magnetic Fe_3O_4 of some multicomponent systems present in synthetic aqueous solutions was performed and metals (Cr, Cu, Ni and Cd) retention varies but the efficiency removal is well over 90%. Removal of Lead ions by $NiFe_2O_4$ nanoparticles was investigated also and results indicated that the removal of Pb at room temperature was 99% under basic condition during one contact [20]. In another development, adsorption of Zn, Cu, and Cd from wastewater by means of maghemite nanoparticles was studied in batch adsorption process and recovery showed that the obtained adsorption data indicated a good adsorption capacity for metal ions removal [32].

Compared with traditional materials, NMs adsorbents have exhibited much higher efficiency, capacity and faster rates in water treatment. It was reported that NMs used as adsorbent for removal of heavy metal ions in wastewater should themselves be non toxic and the nanosorbent should have relatively high sorption capacity and selectivity to low concentration of pollutants. Also, the adsorbed pollutants should be removed from the surface of the nanosorbent easily and the sorbent should be infinitely recycled [2].

4.0 Dyes as Pollutants and Sources

Dyes are complex organic compounds which are used by various industries to colour their products. These dyes are raw materials for various industrial applications such as textile, cosmetics, paper, leather, rubber, carpet, plastic, food, paint and printing industries. Dyes could be natural or synthetic. Wastewater effluents from industries contain dyes which may cause potential hazards to the environment. Some of these dyes are toxic, carcinogenic and can cause skin and eye irritation. The textile industries are the key industries which discharge dyes such as Colour Black G, Congo red, Malachite Green, Methylene Blue, Methyl Orange etc into the environment especially the water body. Such pollutants have greatly affected and reduced aquatic organisms.

4.1 Adsorption of Dyes by Nanomaterials

The effective removal of dyes from industrial effluents and wastewater is of great concern in contemporary times due to the present industrial revolution. Wastewater containg these dyes are difficult to treat using conventional methods since they are stable to light, oxidizing agents and aerobic digestion. Many removal techniques have been applied but adsorption process using NMs have proved to be most effective and efficient as reported by various researchers (Table 2.0). Powdered Fe_2O_3 has been used for dye removal of colour from textile dye wastewater by batch experiment [21]. Nanohybrid graphene oxide and Azide modified Fe_3O_4 nanoparticles were fabricated using Click reaction. The adsorption capacities in the studied concentration range were very high for Methylene Blue and Congo red [22]. In the adsorption removal of Crystal Violet, a carcinogenic textile dye, from aqueous solution by conducting polyaniline/Hollow manganese Ferrite nanocomposite, 95% of Crystal Violet was adsorbed and removal efficiency might be increased by using more weights adsorbent in proportional volume of various concentrations [23]. TiO_2 nanoparticles also showed high efficiency in removal of Malachite Green dye, about 65% of dye removal in the dark while irradiation of the dye increased the removal percentage to 80% [24].

5.0 Factors affecting the adsorbent/adsorbate interactions

5.1 Molecular size

The molecular size has some implications on the adsorption process. The molecules with a suitable size would be adsorbed more favourably since they have more contact sites with the nanoparticles surface. On the contrary, if the molecular size is relatively large, it will have difficulties in moving within pores with size not large enough, according to the so called steric effects. The steric effects are possibly caused by the following reasons: some extremely low size pores might be inaccessible for big molecules; the interior part of the pores might not be reached due to the blockage of the adsorbed molecules; the molecules could not be so com

pact in pores due to the introduction of the substituent group (Mohammed, 2011).

5.2 Solubility

Both solubility and chemical structure of organics are factors of major importance in adsorption. On one hand, it is evident that the more the solubility in water the lower the adsorption capacity of a given compound. The dissolution of adsorbate usually relates to its polarity; the more polar adsorbate has higher solubility in a polar solution (Mohammed, 2011).

5.3 Hydrophobicity

Hydrophobic compounds tend to be pushed to the adsorbent surface and hence they are

Table 1.0: Nanaomaterials and their adsorption capacities at different conditions for various dyes adsorption

S/N	Nanaomaterial	Analyte	pH	Temperature	Adsorption time	Adsorption (%)	Adsorption capacity (mg/g)	Reference
1	Novel Ag/kaoline nanocomposite	Acid Cyanine 5R	3	60	60	90	12.65	[37]
2	Alumina nanoparticle	CBT	2	45	4.5 hrs	25.6	263.16	[35]
3	Fe_3O_4 nanopaticle	Prociom dye	6	25	30 min	24.4	30.503	[21]
4	CuO nanopaticles	Methylene Blue	x	X	6 min	88.93	x	[40]
5	Silver nanopaticle loaded on activated carbon	Methyl Orange	5	25	15 min	98.75	32.99	[42]
6	Nanoaluminium hydroxide	Methyl Violet	10	25	30 min	x	x	[36]
7	Polyaniline/ hollow $MnFe_2O_4$ nanaocomposite	Crystal Violet	7	X	15 min	75.6	x	[23]
8	Surface coated magnetite nanoparticles	Nyloset yellow, E-RK Dye	10	X	1 min	x	136	[28]
9	TiO nanoparticles	Malachite Green	x	30	30 min	80	6.3	[24]
10	Pectin-cerium taungstate	Methylene Blue	8	25	60 min	75	x	[43]

11	Feric oxide	Colarane Blue	2	X	X	94	x	[21]
12	Clicking grapheme oxide/ Fe_3O_4 nanoparticles	Metylene Blue	x	25	20 min	x	109.5	[22]
13	Clicking grapheme oxide/ Fe_3O_4 nanoparticles	Congo Red	x	25	20 min	x	98.8	[22]
14	Nikel oxide nanoparticles	Congo Red	2	27	25 min	x	10.1	[29]

X = undocumented

more adsorbed than hydrophilic compounds. In aqueous solution, the adsorbate with higher hydrophobicity has stronger tendency to be adsorbed and retain on the carbon surface or in the pores (Mohammed, 2011).

5.4 Solution pH

The PH is an important parameter and has been used in the adsorption process in several works. The initial pH of adsorption medium is associated to the adsorption mechanism onto the adsorbent surface from water. When applying the adsorption technique, one of the key parameter to study is the pH, as the pH is responsible for the controlling process (Terrance, 2016) Acidic or alkali species may change the surface chemistry of the adsorbent by reacting with the surface groups. These effects may lead to significant alterations in the adsorption equilibrium depending on the pH. The functional groups exhibit pH-dependent interactions with water, which result in the transformation of the active sites. The removal of acidic/basic species may thus give rise to a concomitant shift in pH of both the medium and the surface. The adsorbate is mainly in protonated form at pH < pKa and in deprotonated form at pH > pKa. These effects may lead to significant alterations in the adsorption equilibrium depending on the pH. Moreover, Amin *et al*., (2014) reported that as the pH of the system increases, the number of negatively charged sites increases which do not favour the adsorption of direct blue-dye anions due to the electrostatic repulsion (Mohammed, 2011).

5.5 Adsorption Dosage

Adsorption dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The amount adsorbed per unit mass of the adsorbent decrease considerably. The decrease in unit adsorption with increase in dosage of adsorbent is due to adsorption sites remaining unsaturated during adsorption process (Mona *et al.*, 2013). The determination of the effect of adsorbent dosage gives an idea about the minimum amount of adsorbent need to be used for adsorption process. This value is usually in the viewpoint of cost. Satisfactory results can be achieved with fewer amounts of nanoparticles sorbent because of higher surface area-to-volume ratio.

5.6 Temperature

Temperature plays key roles on the adsorption process. First, increasing the temperature decreases the viscosity of the solution which, in turn, enhances the rate of diffusion of the adsorbate molecules across the external boundary layer of the adsorbent and resulted in higher adsorption. Second, changing the temperature may affect the equilibrium adsorption capacity of the adsorbent. For instance, the adsorption capacity will decrease upon increasing the temperature for an exothermic reaction; while it will increase for an endothermic one. Hence, a study of the temperature-dependent adsorption processes provides valuable information about the standard Gibbs free energy, enthalpy and entropy changes accompanying adsorption (Mona *et al.*, 2013).

6.0 ADSORPTION ISOTHERM MODELS

Adsorption isotherm gives the explanation on how adsorbent and adsorbate interact with each other and therefore vital in optimizing the use of adsorbents. Various adsorption isotherm models available to describe the equilibrium of adsorption, including Langmuir, Freundlich, BET, Toth, Tempkin, Redlich-Peterson, Sips, Frumkin, Harkins-Jura, Halsey, Henderson and Dubinin–Radushkevich isotherms (Nirmala, 2014). According to the majority of reviewed papers, Langmuir and Freundlich isotherm models were mostly used.

6.1 Langmuir Adsorption Isotherm model

Langmuir adsorption isotherm model assumes monolayer adsorption and adsorption takes place at specific homogeneous sites within the adsorbent. All the sites are considered as identical and energetically equivalent.

Once adsorbate molecule occupies a site, no further adsorption can take place in the same site [9].The Langmuir equation can be expressed as follows:

Non-linear equation;

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

Linear equation;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a C_e} \quad (2)$$

Where, q_e is the amount of adsorbate adsorbed at the time of equilibrium in mg/g, C_e is the equilibrium concentration of adsorbate in the solution in mg/L, q_m is the maximum adsorption capacity in mg/g and K_a is the Langmuir isotherm constant in L/mg.

6.2 Freundlich adsorption isotherm model

Freundlich isotherm model reflects the multilayer adsorption and applicable for heterogeneous adsorption surfaces. This model assumes that;

(i) Several layers of adsorbate can be attached on the adsorbent and adsorbate will continuously keep binding to the adsorbent;

(ii) The energy required for adsorption is not constant, but it varies and exponentially distributed.

This model can be represented by below equations.

Non-linear equation;

$$q_e = K_f C_e^{1/n} \quad (3)$$

Linear equation;

$$\log q_e = log K_f + \frac{1}{n}(log C_e) \quad (4)$$

Where qe is the amount of adsorbate at equilibrium time in mg/g, C_e is the equilibrium concentration of adsorbate in the solution in mg/L, K_f is the capacity of the adsorbent in mg/g and n is the adsorption constant for freundlich in L/mg, usually greater than one. It can be stated that, if the 1/n value is below unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favourable physical process [9].

7.0 Adsorption Kinetic Models

The rate and mechanism of adsorption processes can be elucidated on the basis of kinetic study [29].The contact time experimental results can be used to study the rate-limiting step on the adsorption process. Several adsorption kinetics models have established to understand the adsorption kinetics and rate-limiting step. The commonly used include Pseudo-First and Pseudo-Second-Order rate models. Others are Weber and Morris sorption kinetics model, external mass transfer model, Adam-Bohart-Thomas relation, First-Order reaction model, First- Order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchie's equation. The model with higher correlation coefficient (r^2) value (close or equal to 1) successfully describes the kinetics of the adsorption of the adsorbate onto the adsorbent [30]. This review takes a look at Pseudo-First and Pseudo-Second-Order and intra-particle Diffusion Model.

7.1 Pseudo-First-Order Kinetics

According to Lagergren Model, the Pseudo-First-Order Kinetics equation is given as;

$$\log(q_e - q_t) = log q_e - \frac{K_1}{2.303}(t) \tag{5}$$

Where q_e and q_t are the mass of adsorbate per unit mass of adsorbent at equilibrium and at time, t respectively in mg/g, K_1 is the rate constant ($L.min^{-1}$). The plot of log (q_e - q_t) verses t gives a straight line for the pseudo-first-order kinetics.

7.2 Pseudo-Second-Order Kinetics

This model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate [30]. The Pseudo-Second-Order equation is given below

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \tag{6}$$

Where K_2 is equilibrium rate constant of Pseudo-Second-Order adsorption ($mg^{-1}min^{-1}$). The plot of t/q_t verses t should give a straight linear relationship that allows the computation of a Second-Order rate constant K_2 and q_e.

7.3 Intra-particle Diffusion Model

This Model is based on the theory proposed by Weber and Morris [30]. The equation is given below;

$$Q_t = K_p t^{0.5} + C \tag{7}$$

Where Q_t is the adsorption capacity (mg/g) at time, t (min), K_p is the diffusion constant ($mg/gmin^{1/2}$) and C (mg/g) is a constant that gives an indication of the thickness of the boundary layer.

8 Conclusions.

Nanotechnology in terms of use of nanomaterials as adsorbents has proven to be efficient and has high capacity for removal of heavy metals and dyes from wastewater and industria l effluents. On the average, the review in this study has shown that, the removal capacity is about

80% for both heavy metals and dyes. Therefore, a lot of research works are needed in the field of nanosience/nanotechnology to effectively design nanomaterials that can be used to increase the percentage performance in terms of removal capacity of pollutants from the environment.

The use of adsorption process should be given maximum attention as a means of pollution control and recycling of industrial wastewater as a result of its effectiveness, easy process and low cost.

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